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Syntheses and spin structures of 1,6-dithiapyrene derivatives having imino nitroxide or oxoverdazyl moiety

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Abstract

1,6-Dithiapyrene (DTPY) derivatives containing imino nitroxide or 1,5-dimethyl-6-oxoverdazyl moiety **1** and **2** have been designed as new neutral radicals, and their syntheses were carried out from DTPY in three steps. The isotropic hyperfine coupling constants of the protons and nitrogen atoms for **1** and **2** were determined by ESR/ENDOR/TRIPLE measurements and ESR simulations. Their assignments were made with the help of the density functional theory by using GAUSSIAN-98 with the UBLYP/6-31G**//UBLYP/6-31G** method. The syntheses of **1** and **2** contribute to the expansion of structural diversity in the field of the magnetic and conductive materials.

Keywords: 1,6-Dithiapyrene; Imino nitroxide; Oxoverdazyl; Spin structure; Density functional theory; ESR/ENDOR/TRIPLE spectroscopy

1. Introduction

Organic molecular magnetism has attracted much attention since the discovery of a purely organic ferromagnet, *p*-nitrophenyl α-nitronyl nitroxide [1]. Recently, development of new stable radicals and the multifunctional molecule with both magnetism and electric conductivity is the focus of current topics in studies of a new intriguing molecule-based material science [1,2]. Efforts to realize ferromagnetic-conducting organic materials have been carried out through the synthetic study of tetrathiafulvalene (TTF) or pyridyl derivatives with stable radicals such as α-nitronyl nitroxide, 2,2,6,6-tetramethylpiperidine-1-oxyl, verdazyl and 6-oxophenalenoxyl (TEMPO) radicals [3]. The theoretical study by *ab initio* molecular orbital calculations has indicated that the organic ferromagnetic metals are feasible in the case of electronically and spatially designed CT complexes of the donor molecule containing a radical substituent [4]. To search such CT complexes, the expansion of structural diversity is an important issue in the field of organic-based magnetic and conductive materials. 1,6-Dithiapyrene (DTPY), a peri-condensed Weitz-type donor, possesses low oxidation potentials similar to those of TTF, and the DTPY–TCNQ complex showed metallic conductivity [5]. Our recent study on an improved synthetic method of DTPY encouraged us to functionalize DTPY [6]. Thus, we have designed new DTPY derivatives containing imino nitroxide, 1,5-dimethyl-6-oxoverdazyl and α-nitronyl nitroxide moieties, **1**, **2** and **3**. This paper deals with the syntheses of **1** and **2**, and the determination of their spin structures by the ESR/ENDOR/TRIPLE measurements and the density functional theory (DFT).

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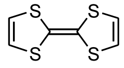

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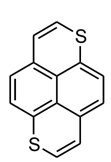

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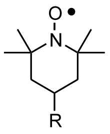
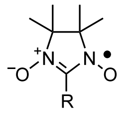
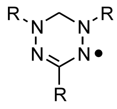


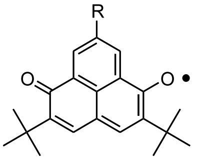
TEMPO



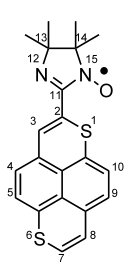
α-Nitronyl nitroxide



Verdazyl



6-Oxophenalenoxyl



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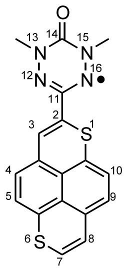

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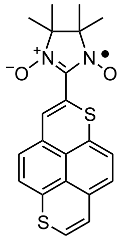

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2. Experimental

2.1. Materials and methods

All solvents were purified according to the standard procedures [7]. All chemicals used in synthesis were of reagent grade and used without further purification. The reaction requiring anhydrous conditions was performed under an argon atmosphere. 2,3-Bis(hydroxylamino)-2,3-dimethylbutane (**5**), 2,4-dimethylcabonohydrazide (**6**) and active PbO_2 were prepared by the reference procedures [8–10]. ^1H NMR spectra were recorded on a JEOL EX-270 spectrometer with Me_4Si as an internal standard. Infrared and electronic spectra were recorded using KBr plates on Perkin Elmer 1600 series FT IR and Shimadzu UV-3100PC, respectively. EI MS spectra were recorded at 70 eV on a Shimadzu QP-5000. Melting points were measured by a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were performed at the Analytical Center of Graduate School of Science, Osaka University. The liquid-phase ESR, ENDOR and TRIPLE spectra were recorded on a Bruker X-band ESR spectrometer ESP300/350. The solutions of the radicals were degassed by freeze-pump-thaw method before the measurements. R_f values on TLC were recorded on E. Merck precoated (0.25 mm) silica gel 60 F_{254} and alumina F_{254} plates. The plates were sprayed with a solution of 10% phosphomolybdic acid in 95% EtOH and then heated until the spots become clearly visible. Silica gel 60 (100–200 mesh) and alumina (ICN, N-super I) were used for column chromatography. Deactivated silica gel and alumina were prepared by mixing with 6% water. All calculations based on DFT were performed by GAUSSIAN-98 and geometries were optimized by using the UBLYP/6-31G** method [11]. The spin density distributions were calculated by using the UBLYP/6-31G** method.

2.2. Synthesis of 2-formyl-1,6-dithiapyrene (4)

A solution of DTPY (150 mg, 0.62 mmol) in THF (15 ml) was cooled at −100 °C. To this solution was added *n*-BuLi (1.5 M hexane solution, 0.42 ml, 0.62 mmol) and the reaction mixture was warmed up to −30 °C over 1.5 h. After being cooled to −85 °C, a chilled (−70 °C) solution of DMF (0.5 ml, 6.5 mmol) in THF (4.5 ml) was added, and the mixture was stirred for 0.5 h at −85 °C. A pH 7 phosphate buffer solution (0.1 M, 15 ml), a saturated NaCl solution (50 ml) and EtOAc (150 ml) were added to the reaction mixture, successively. The resulting black precipitates were removed by filtration and the filtrates were extracted with EtOAc (30 ml). The organic layer was washed with a saturated NaCl solution (40 ml × 2) and water (30 ml), dried over Na_2SO_4 and filtered. The EtOAc solution was directly subjected to silica gel flash column chromatography with EtOAc as eluant and concentrated under reduced pressure, to give dark green powder **4** (145 mg, 87%). M.p. 215–216 °C; $R_f = 0.47$ (silica gel, hexane:ethyl acetate = 2:1); ^1H NMR ($CDCl_3$) δ 5.62 (1H, d, $J = 10$ Hz), 5.85 (1H, d, $J = 10$ Hz), 6.15 (1H, d, $J = 7.7$ Hz), 6.27 (1H, d, $J = 7.9$ Hz), 6.28 (1H, d, $J = 7.7$ Hz), 6.37 (1H, d, $J = 7.9$ Hz), 6.47 (1H, s), 9.11 (1H, s); EI MS *m*/*z* (rel intensity) 268 (M^+, 100%); IR (KBr) 3057, 1663 cm^{-1}; UV (KBr) 624, 460, 414 nm; *Anal*. Calc. for $C_{15}H_8S_2O$: C, 67.14, H, 3.00%. Found; C, 66.66, H, 3.18%.

2.3. Synthesis of 1,3-dihydroxy-2-(1′,6′-dithiapyrene-2′-yl)-4,4,5,5-tetramethylimidazolidine (7)

The formyl derivative **4** (100 mg, 0.37 mmol), bis(hydroxylamine) **5** (74 mg, 0.43 mmol) and *p*-toluenesulfonic acid monohydrate (7.0 mg, 0.036 mmol) were placed in a Schlenk tube equipped with reflux condenser and dissolved with benzene (6 ml), and stirred at 80 °C. After being mixed for 12 h, **5** (80 mg) was added and the mixture was further stirred for 22 h at 80 °C. After being cooled to room temperature (r.t.), benzene (50 ml) was added to the mixture. The organic layer was washed with a saturated NaCl solution (20 ml × 2) and water (20 ml), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residual brown powder was subjected to alumina column chromatography with a 20:1–3:1 mixture of hexane and ethyl acetate as eluant, to give orange powder **7** (67 mg, 47%). M.p. 208–209 °C; $R_f = 0.47$ (alumina, hexane:ethyl acetate = 2:1); ^{1}H NMR ($CDCl_3$) δ 1.04 (3H, s), 1.06 (3H, s), 1.07 (3H, s), 1.20 (3H, s), 4.04 (1H, bs), 5.52 (1H, d, $J = 10$ Hz), 5.73 (1H, d, $J = 10$ Hz), 5.89 (1H, s), 6.01 (1H, d, $J = 7.6$ Hz), 6.02 (1H, d, $J = 7.8$ Hz), 6.19 (1H, d, $J = 7.6$ Hz), 6.28 (1H, d, $J = 7.8$ Hz).

*2.4. Synthesis of hexahydro-1,5-dimethyl-3-(1′,6′-dithiapyrene-2′-yl)-6-oxo-1,2,4,5-tetrazine (**8**)*

The formyl derivative **4** (150 mg, 0.56 mmol), the urea derivative **6** (92 mg, 0.56 mmol) and *p*-toluenesulfonic acid monohydrate (5.0 mg, 0.026 mmol) were placed in a Schlenk tube and dissolved with CH_2Cl_2 (30 ml), and stirred at r.t. for 23 h. The brownish orange powder was removed by filtration, and a saturated $NaHCO_3$ solution was added to the resulting filtrates and the products were extracted with CH_2Cl_2 (30 ml). The organic layer was washed with a saturated $NaHCO_3$ solution (30 ml) and a saturated NaCl solution (30 ml), successively. The CH_2Cl_2 solution was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residual dark red solid was reprecipitated from about a 1:1 mixture of hexane and CH_2Cl_2 solution at −30 °C, to give reddish brown powder **8** (45 mg, 22%). $R_f = 0.56$ (silica gel, THF); ^{1}H NMR ($CDCl_3$) δ 3.22 (3H, s), 3.24 (3H, s), 4.60 (2H, bs), 5.66 (1H, d, $J = 10$ Hz), 5.89 (1H, d, $J = 10$ Hz), 6.11 (1H, s), 6.18 (1H, d, $J = 7.7$ Hz), 6.24 (1H, d, $J = 7.9$ Hz), 6.34 (1H, d, $J = 7.7$ Hz), 6.46 (1H, d, $J = 7.9$ Hz), 7.06 (1H, s); EI MS *m/z* (rel intensity) 368 (M^+, 100%).

*2.5. Synthesis of 2-(1′,6′-dithiapyrene-2′-yl)-4,4,5,5-tetramethyl-1-oxylimidazoline (**1**)*

Bis(hydroxylamine) **7** (1.0 mg, 0.0026 mmol) was placed in a Schlenk tube and dissolved with toluene (1 ml). To this mixture was added active PbO_2 (16 mg, 0.067 mmol) and stirred at r.t. for 0.5 h. The resulting solid was filtered through the celite column, rinsed with toluene. The filtrates were concentrated under reduced pressure, to give dark green powder **1** (1.0 mg, 100%). $R_f = 0.43$ (silica gel, hexane:ethyl acetate = 2:1); IR (KBr) 2930, 1561, 1198 cm^{-1}; UV (KBr) 404 nm; EI MS *m/z* (rel intensity) 379 (M^+, 7%), 239 ($M^+ - C_7H_{12}N_2O$, 37%).

*2.6. Synthesis of 2-(1′,5′-dimethyl-6′-oxoverdazyl-3′-yl)-1,6-dithiapyrene (**2**)*

Tetrazine **8** (1.0 mg, 0.0027 mmol) was placed in a Schlenk tube and dissolved with THF (1 ml). To this mixture was added active PbO_2 (13 mg, 0.054 mmol), and stirred at r.t. for 1 h. The resulting solid was filtered through the celite column, rinsed with THF. The filtrates were concentrated under reduced pressure, to give dark red powder **2** (1.0 mg, 100%). $R_f = 0.74$ (silica gel, THF).

3. Results and discussion

*3.1. Syntheses of **1** and **2***

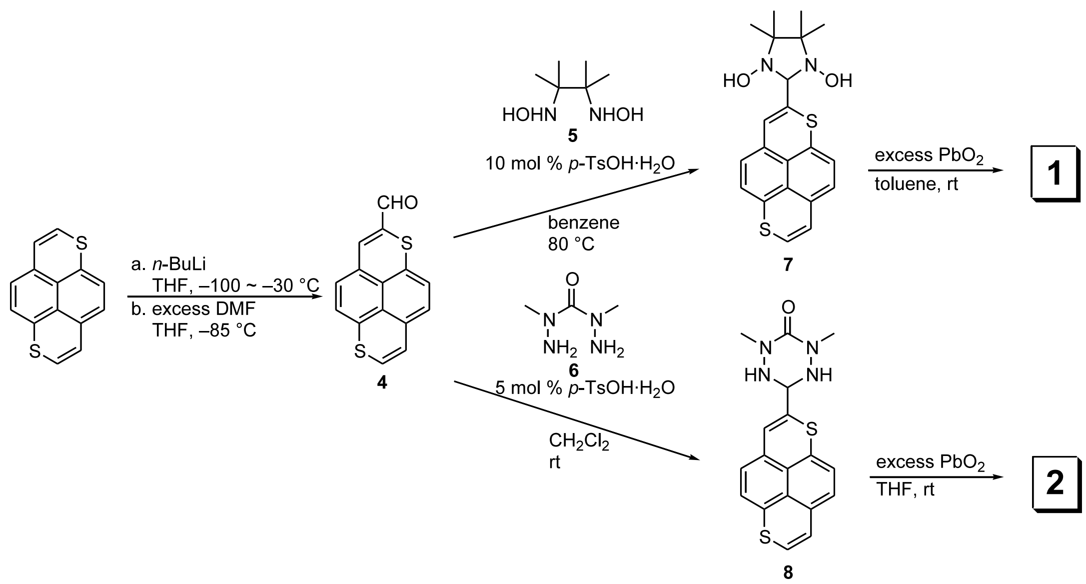
The target molecules **1** and **2** were synthesized from DTPY in three steps, respectively, (Scheme 1). The formylation of DTPY to **4** was performed by the treatment of *n*-BuLi followed by DMF. The radical precursors **7** and **8** were synthesized from **4** by the condensation with **5** and **6**, respectively, in the presence of a catalytic amount of *p*-toluenesulfonic acid monohydrate. The radicals **1** and **2** were obtained by the treatment of a large excess amount of active PbO_2 at r.t. The radicals **1** and **2** are isolable in the solid state in an air atmosphere, but most of the radicals decompose in a day at r.t. under an argon atmosphere. In a degassed toluene at −30 °C, both radicals are stable for a long period of time, but decompose under an air atmosphere.

An α-nitronyl nitroxide derivative of DTPY **3** was also obtained by the treatment of **7** with active PbO_2 in the presence of K_2CO_3 in THF at −78 °C, but this radical was unstable and detectable only as the mixture with the imino nitroxide derivative **1** judging from the ESR spectroscopy. The ESR signal of **3** disappeared in a day at r.t. while the signal intensity of **1** increased, being indicative of the transformation of the α-nitronyl nitroxide **3** to the imino nitroxide **1** in the reaction media.

3.2. ESR, ENDOR and TRIPLE spectroscopies

*3.2.1. Spectroscopies of **1***

Fig. 1(A) shows a hyperfine ESR spectrum observed for **1** in toluene (1.0×10^{-4} M). In the ENDOR spectrum shown in Fig. 1(B), the innermost intense pair signals (whose separation is 0.43 MHz) are attributed to the protons of the methyl groups on the imino nitroxide moiety due to its hyperfine coupling constant (hfcc) and the high signal intensity compared with those of other proton and nitrogen atoms [12]. In addition, another pair seen at 13.63 and 15.20 MHz is likely to be attributed to a proton on the DTPY moiety. Fig. 1(C) shows a pair of signals assignable to the ^{14}N-ENDOR transitions, which is attributed to a nitrogen atom of the imino nitroxide [13]. A pair of the signal due to the nitroxyl nitrogen atom was observed at approximately 12 and 14 MHz, although the signal at the higher frequency overlapped with the signals due to the methyl protons (shown in Fig. 1(B)). The TRIPLE spectrum (Fig. 1(E)) indicated that the relative signs of the hfcc of the proton on DTPY moiety and that of the nitroxyl



Scheme 1. Synthetic methods of **1** and **2** from DTPY.

nitrogen atom were the same. The signs of the other hfccs were not experimentally determined. The spectral simulation (Fig. 1(D)) was made on the basis of the isotropic hfccs of two kinds of nitrogen atoms and two kinds of protons obtained in the ENDOR/TRIPLE spectra.

3.2.2. *Spectroscopies of* **2**

Fig. 2(A) shows a well-resolved hyperfine ESR spectrum observed for **2** in toluene (1.0×10^{-3} M). In Fig. 2(B), the outermost pair signals due to protons of two methyl groups and two pairs of signals due to two kinds of nitrogen atoms on the oxoverdazyl moiety were observed. In addition, as shown in Fig. 2(C), two pairs of proton signals were observed, which are likely attributable to protons on the DTPY moiety. Except for the hfcc of the nitrogen atom with a larger magnitude, the relative signs of the hfccs were determined by the TRIPLE spectroscopies (Fig. 2(E and F)), indicating that all the hfccs have the same sign. The

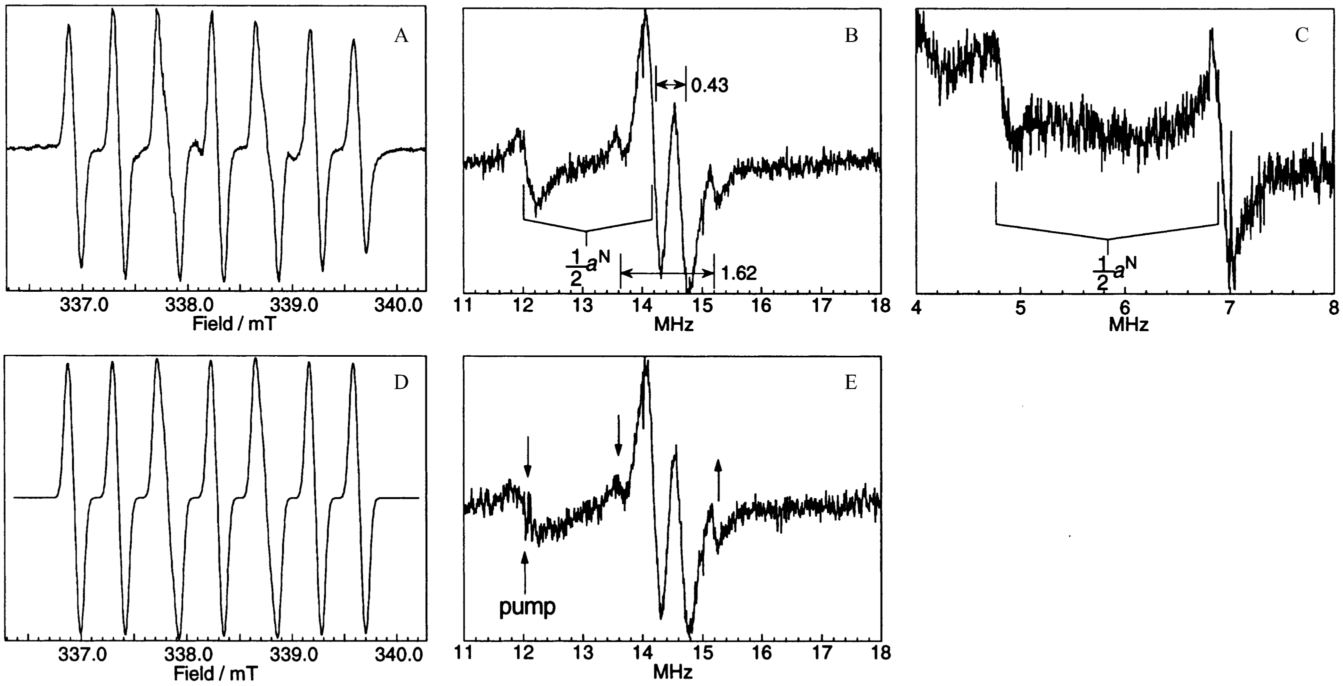


Fig. 1. Observed ESR (A), ENDOR (B and C) and TRIPLE spectra (E; pump frequency, 12.08 MHz) for **1** in toluene (1×10^{-4} M) at 290 K; microwave frequency was 9.4855450 GHz and simulated ESR spectrum (D).

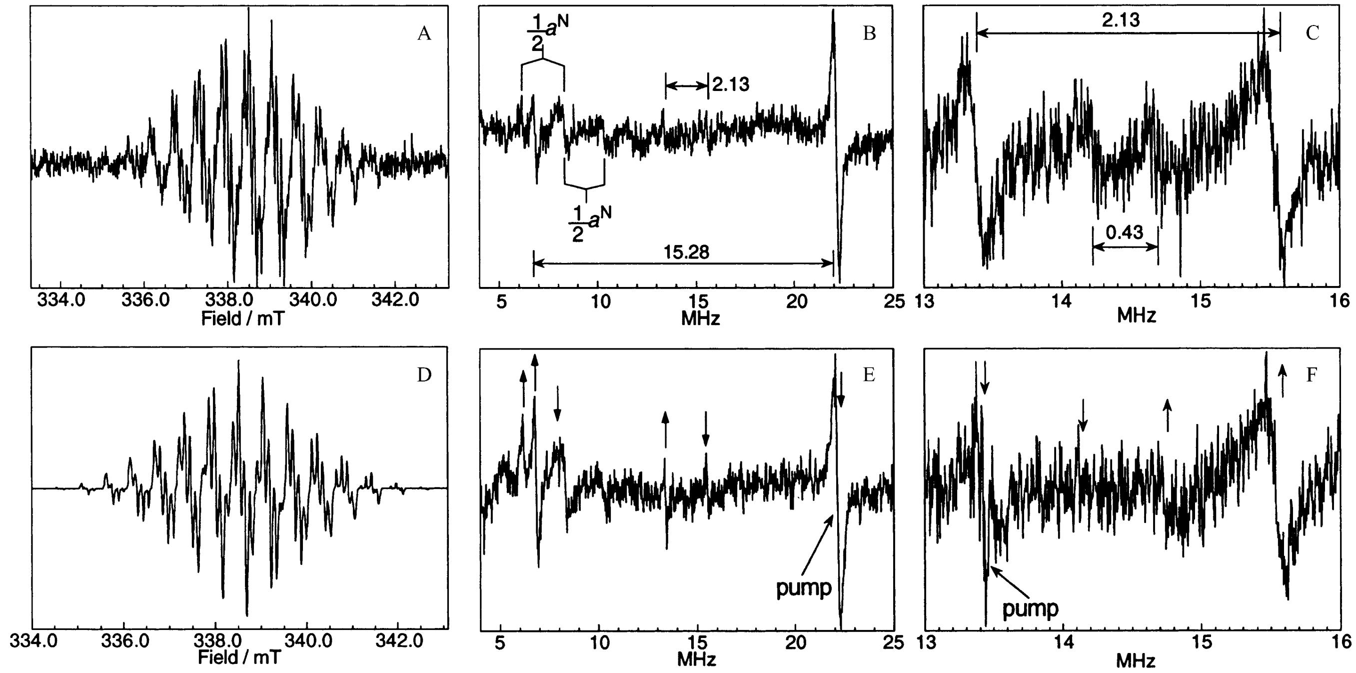


Fig. 2. Observed ESR (A), ENDOR (B and C) and TRIPLE spectra (E and F; pump frequency, 22.03 and 13.38 MHz, respectively,) for **2** in toluene (1×10^{-3} M) at 290 K; microwave frequency was 9.4822410 GHz and simulated ESR spectrum (D).

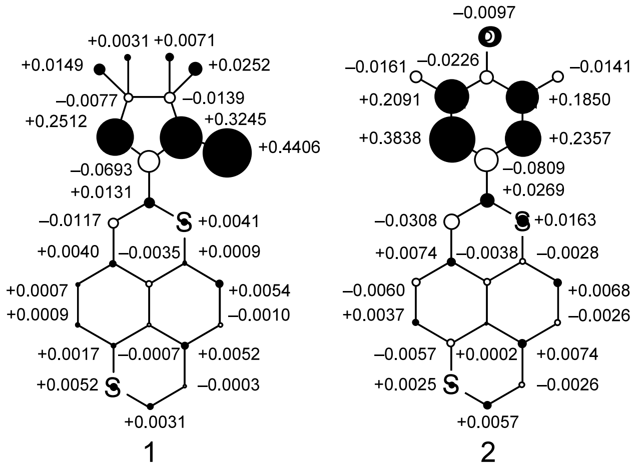


Fig. 3. Spin density distributions of **1** and **2** calculated by the DFT calculation by using GAUSSIAN-98 with the UBLYP/6-31G**// UBLYP/6-31G** method. Vacant and filled circles denote negative and positive spin densities, respectively.

spectral simulation (Fig. 2(D)) was satisfactorily made on the basis of the isotropic hfccs of two kinds of nitrogen atoms and four kinds of protons obtained by ENDOR/TRIPLE spectroscopies with the additional one proton hfcc (0.0420 mT).

3.3. *Density functional calculations*

To assign the hfccs of the proton(s) on the DTPY moiety for **1** and **2**, the spin density distributions of **1** and **2** were calculated by using GAUSSIAN-98 in terms of UBLYP/6-31G**//UBLYP/6-31G** method (Fig. 3). In the optimized structures of **1** and **2**, the DTPY moieties are almost coplanar with the imino nitroxide or oxoverdazyl moieties. The calculations indicate that the unpaired electron distributes slightly to the DTPY moiety in **1** and **2**, which is consistent with the fact that the relatively small hfccs were observed in the ENDOR spectra for **1** and **2**. The assignments were made on the basis of the calculations and summarized in Table 1. The hfcc (+0.058 mT in experimental) due to a proton on the DTPY moiety in **1** was assigned to the 3-position. The two hfccs due to protons on the DTPY moiety in **2**, which were observed in the ENDOR spectra, are assigned to the 3- and 4-positions in consideration of the experimental results that their relative signs were the same. Finally, the hfcc of the proton, which was added for the spectral simulation for **2**, is likely to either 7- or 10-position judging from its magnitude. The agreements between the experimental values and calculated ones are satisfactory.

4. Conclusion

In conclusion, the DTPY derivatives **1** and **2** having imino nitroxide or oxoverdazyl were synthesized. The hfccs and relative signs of the protons and nitrogen atoms for **1** and **2** were determined by the ESR/ENDOR/TRIPLE measurements and DFT calculations. The syntheses of the DTPY donors containing an imino nitroxide or oxoverdazyl moiety serve for the

Table 1
The experimental and calculated hfccs of the protons and nitrogen atoms for **1** and **2**

Compound	Experimental calculation	a_H/mT		a_N/mT		g-Value		
		3	13, 14 (CH$_3$)	12	15			
1		$+0.058^{a,b}$ $+0.037^{c}$ ($+0.034^{d}$)	$0.015^{a,e}$ $+0.006^{c}$	$0.419^{a,e}$ $+0.380^{c}$	$+0.933^{a,b}$ $+0.637^{c}$	2.0062		
		a_H/mT				a_N/mT		g-Value
		3	4	7 or 10	13, 15 (CH$_3$)	12, 16	13, 15	
2		$+0.077^{a,b}$ $+0.068^{c}$ ($+0.089^{d}$)	$+0.018^{a,b}$ $+0.012^{c}$ ($+0.017^{d}$)	$0.042^{e,f}$ -0.016^{c} or -0.014^{c} (-0.020^{d}or -0.017^{d})	$+0.545^{a,b}$ $+0.528^{c}$	$0.655^{a,e}$ $+0.533^{c}$	$+0.518^{a,b}$ $+0.372^{c}$	2.0039

[a] The hfccs were determined by ENDOR spectra in toluene at 290 K.
[b] The relative signs of the hfccs were determined in terms of the TRIPLE spectroscopy.
[c] The hfccs were calculated by using GAUSSIAN-98 with UBLYP/6-31G**//UBLYP/6-31G** method.
[d] The hfccs were calculated by using GAUSSIAN-98 with UBLYP/6-31G**//UBLYP/6-31G** method with the help of McConnell's equation ($Q = -2.90$ mT).
[e] The relative signs of the hfccs were experimentally unknown.
[f] The hfcc was determined by the simulated ESR spectrum.

expansion of structural diversity in the field of the magnetic and conductive materials science. The stabilization of the radical derivative of DTPY and preparation of CT complexes with electron-deficient molecules are in progress.

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